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Compositions based on thermoplastic semicrystalline resins and block copolymers, resulting materials and methods for obtaining same.

This invention concerns compositions based on semicrystalline thermoplastic polymers, the materials obtained from these compositions and the methods for obtaining them. Easy to use and transform, thermoplastic resins are widely used in numerous fields based on their own mechanical and chemical properties.

Among semicrystalline thermoplastic resins we find polyamides (PA), polyolefins, fluorinated resins, vinyl resins, polyesters, polycarbonates, polyoxyalkalenes, polyurethanes and polysiloxanes.

However, since their mechanical, chemical and/or thermal properties are not always sufficient, particularly their shock resistance at ambient and/or low temperature and their elongation at break, it is often necessary to add specific additives to them.

To improve certain properties, particularly shock resistance, we can add plasticizers that lower the intermolecular interaction strength and reduce the modulus and therefore soften the polymer to which they are added, which is not necessarily desired for certain applications. Furthermore, these substances have the well known disadvantage of exuding relatively quickly some of the polymer material into which they were incorporated, which therefore results in a reduction in shock resistance and is sometimes accompanied by shrinkage of the material.

Elastomers and/or thermoplastic elastomers (TPE) have also been suggested as impact additives as described in EP 239707. The compositions thus obtained have improved shock resistance compared to thermoplastic resin alone, but it is necessary to incorporate a large quantity of elastomers or TPE in the composition to obtain a notable improvement of these properties, typically on the order of 20% by weight

of the total mass of the composition, and this adversely affects the intrinsic properties of the semicrystalline thermoplastic resin.

According to the prior art, when standard shock resistance or other additives are added to a thermoplastic resin, the domains formed by these additives tend to consolidate with one another in the resin. This phenomenon, harmful to the properties of the final material obtained by forming the composition, is called coalescence.

Another known technical solution consists of combining another polymer with the thermoplastic resin whose properties are to be improved through alloying. However, mixing polymers with different chemical natures is often difficult given the incompatibility that may exist between the resins that are to be combined; this incompatibility results in a macroseparation of phases that, if not controlled, can lead to materials with coarse properties and therefore poor mechanical properties. To solve this problem, we add what is called a compatibilizing agent that positions itself in the interface between the incompatible polymers: the role of the compatibilizing agent is to reduce the size of the distinct phases to a few micrometers while limiting coalescence. The addition of compatibilizing agents (or their *in situ* synthesis) both reduces the size of the domains made up by the second polymer dispersed in the matrix consisting of the first polymer and improves the cohesion between these domains and the matrix. Compatibilizing agents (block copolymer(s)) for incompatible resins are described in DE 4416853 and DE 4416855, for example. However, for numerous applications, this method does not produce materials with the required mechanical and chemical resistance properties.

Patent US-A-5484838 discloses a mixture of at least two polymers chosen from a collection of polymers. These polymers include the block polymer styrene-butadiene and the block copolymer methylmethacrylate styrene-butadiene. For the person skilled in the art, the first copolymer is recognized as a diblock where each of the blocks is separated by a hyphen. Likewise, for the same reason the

second block copolymer is recognized as being a diblock where each of the blocks is separated by a hyphen and is made up of a block formed by methyl methacrylate monomers and styrene and a polybutadiene block.

Patent application JP-A-63-308655 describes a composition based on poly(vinylidene difluoride) (PVDF) comprising an A-B diblock, an A-B-A triblock or star-shaped A-B block copolymer depending on the number of dithiocarbonate groups of the radical primer used to synthesize the copolymer.

The monomer(s) used to synthesize the A block compatible with PVDF are chosen from methyl methacrylate, methyl acrylate and vinyl acetate.

Preferably, the B block has a vitreous transition temperature T_g that not does exceed 0°C and better still, does not exceed -10°C .

Based on these T_g values, the monomer destined to form the B block is selected based on the known T_g values of the homopolymers with a molecular weight of at least 10,000 obtained through standard radical polymerization. Thus, ethyl acrylate results in this type of homopolymer with a $T_g = -24^\circ\text{C}$. The proposed list contains: butyl acrylate (-54°C), 2-ethylhexyl acrylate (-85°C), hydroxyethyl acrylate (-15°C) and 2-ethylhexyl methacrylate (-10°C).

The B block may also consist of several monomers chosen based on the T_g of their corresponding homopolymer and in calculable proportions in order to obtain a T_g for the B block copolymer that does not exceed 0°C .

The block copolymer contains 5 to 75% by weight of block A compared to the total weight, and the composition preferably contains 5 to 30 parts of the block copolymer per 100 parts by weight of PVDF.

This PVDF-based composition (Kynar 740®) is described as having improved properties compared to PVDF alone, particularly with respect to flexibility, shock resistance, tensile strength and elongation at break.

However, this prior art composition has disadvantages. First of all, the dithiocarbonate radical primer contains sulfur, and this composition has a tendency to turn yellow. Furthermore, examples 1 to 5

show that in block copolymer synthesis, homopolymer(s) with contents of 13 to 18% is/are formed. These homopolymers can be extracted from the diblock with acetone. Finally, if the B block is incompatible with PVDF, since it is by nature elastomeric, it forms discrete soft areas. These soft areas make the composition softer than PVDF alone. In other words, the limit or maximum use temperature of the composition characterized by the Vicat temperature is reduced, and this is a considerable disadvantage.

Patent JP-B-46-7457 describes a composition based on poly(vinyl chloride) (PVC) comprising an A-B diblock block copolymer.

The A-B diblock is obtained through live anionic polymerization of the B block, then the A block.

The monomer used to synthesize the elastomeric B block is a diene chosen from butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 2-phenyl-1,3-butadiene.

The monomer used to synthesize the A block from the live B polymer is methyl methacrylate (MMA).

The A diblock copolymer is therefore poly(MMA)-poly(diene) and contains 20 to 80% by weight poly(MMA) and 80 to 20% by weight poly(diene).

It is indicated that the poly(MMA)-poly(diene) diblock copolymer contains a small quantity of polydiene homopolymer and that it is possible to remove this homopolymer through extractions using a solvent such as petroleum ether or cyclohexane.

The material obtained from the PVC composition containing this poly(MMA)-poly(diene) diblock is described as having better properties than a material obtained using a PVC composition mixed with an elastomer formed by a statistical copolymer.

Shock resistance, tensile strength and transparency are increased selectively. On the other hand, the hardness (Rockwell R) of the different materials of table 1 is inferior to that of unmodified PVC, and the higher the diblock copolymer content, the more the hardness of the material decreases.

Table 1 also shows a decrease in transparency and an increase in turbidity (Haze) as the diblock copolymer content increases.

This situation is bothersome for users of the material obtained from the PVC + poly(MMA)-poly(diene) mixture because the idea is to improve shock resistance without decreasing hardness or without reducing the use temperature range of the material. This temperature range is characterized by the Vicat temperature or Vicat point.

The first goal of this invention is to offer compositions containing:

- a semicrystalline thermoplastic resin X_1 or several compatible thermoplastic resins X_1 to X_n where at least one X_1 is semicrystalline, and
 - at least one block copolymer (sequences);

- n being a whole number equal to or greater than 1,

leading, through molding, to materials or objects having good hardness and shock resistance and improved elongation at break, resistance to stress cracking and deformation and thermal resistance (use temperature range) compared to the semicrystalline resin(s) alone or mixed with additives known in the prior art.

The problem above is raised in particular for thermoplastic halogenated polymers or copolymers, particularly PVDF, PVC or chlorinated PVC (CPVC).

Additionally, the applicant has found that the PVDF or PVC-based compositions described above and containing A-B or A-B-A diblocks or star-shaped A-B diblocks have a major disadvantage in that they contain A or B homopolymer by-products from the synthesis of these blocks: the presence of homopolymers is particularly harmful for the mechanical properties of the material, especially with respect to their Vicat hardness and particularly their tractive behavior.

The documents cited above potentially provided for purification of the block copolymers at the end of their synthesis via selective solvent extraction (acetone, petroleum ether or cyclohexane). This extraction step is both costly and tedious, and is a notable disadvantage in the industrial implementation of the teaching of the two Japanese documents mentioned above.

Thus, a second goal of this invention is to find a technical solution to the problem presented above that does not require selective solvent extraction and that therefore offers highly simplified industrial feasibility.

The first goal is achieved by a composition intended to be formed into a material or an object comprising:

- a semicrystalline thermoplastic resin X_1 or several compatible thermoplastic resins X_1 to X_n at least one of which is semicrystalline, and
- at least one block copolymer (sequences),
- n being a whole number equal to or greater than 1,

characterized in that:

- the block copolymer comprises at least three blocks A, B and C connected to one another in this order, each block being either a homopolymer or a copolymer obtained with two or three monomers, the A block being connected to the B block and the B block to the C block by means of a covalent bond or an intermediate molecule connected to one of these blocks via a covalent bond and to the other block via another covalent bond and in that:

- the A block is compatible with the thermoplastic resins X_1 to X_n ,
- the B block is incompatible with the thermoplastic resins X_1 to X_n and incompatible with the A block,
- the C block is incompatible with the thermoplastic resins X_1 to X_n the A block and the B block.

In general, the B block has a vitreous transition temperature $Tg_{(B)}$ lower than 23°C.

Advantageously, the $Tg_{(B)}$ of the B block is lower than 0°C.

Preferably, the $T_{g(B)}$ of the B block is lower than -50°C .

The selection of the temperature $T_{g(B)}$ depends on the temperature T_p likely to be taken on by the material or the object obtained from the composition according to the invention at the time of their use. Effectively, at this temperature T_p , it is preferable for the B block to be elastomeric and not in vitreous state.

Preferably, the C Block has a vitreous transition temperature $T_{g(C)}$ or a melting temperature $T_{f(C)}$ higher than the $T_{g(B)}$ of the B block.

This characteristic offers the possibility for the C block to be in vitreous state or in a partially crystalline state and for the B block to be in elastomeric state for a same use temperature T_p .

According to this invention, it is possible to select the nature of the B blocks so that they have a certain $T_{g(B)}$ and thus, at the use temperature T_p of the material or the object formed from the composition, to have an elastomeric or supple state for these B block polymers. On the other hand, as the block C polymers may have a $T_{g(C)}$ or a T_f higher than the $T_{g(B)}$ they may be in relatively rigid vitreous state at the same use temperature.

Since the C blocks are incompatible with the thermoplastic resin(s), the A blocks and the B blocks, they form a discrete rigid phase inside the material by forming nanodomains included in the material and serving as anchorings near one of the ends of each B block. The other end of each B block is connected to an A block that has a strong affinity with the semicrystalline thermoplastic resin or resins. This strong affinity provides a second anchoring near the second end of the B block.

The compatibility of the A blocks and the above-mentioned incompatibilities of the B and C blocks with the selection of the $T_{g(B)}$, the $T_{g(C)}$ or the $T_{f(C)}$ of the composition according to the invention make the elastomeric or soft B blocks more effective with respect to the shock resistance properties of the material while at the same time making it possible to preserve or even improve the hardness of the material. We note the conservation of or increase in the Vicat temperature of the material formed from the composition compared to the material formed from semicrystalline thermoplastic resin or from the mixture of semicrystalline thermoplastic resins.

The B block of an ABC copolymer is considered compatible with the semicrystalline thermoplastic resin if the A polymer identical to this block (and thus without B and C sequences) is compatible with this resin in melted state. Likewise, the A and B blocks are considered compatible if the A and B polymers identical to these blocks are compatible. In general, compatibility between two polymers means that one is able to dissolve in the other in melted state or that they are completely miscible.

Otherwise, the polymers or blocks are called incompatible.

The lower the mix enthalpy of two polymers, the greater their compatibility. In certain cases, there is a favorable specific interaction between the monomers that results in a negative mix enthalpy for the corresponding polymers. In the context of this invention, the use of compatible polymers whose mix enthalpy is negative or nil is preferred.

However, the mix enthalpy cannot be measured using standard methods for all polymers, and therefore the compatibility can only be determined indirectly, for example by means of viscoelastic analysis during torsion or oscillation or by means of differential calorimetric analysis.

For compatible polymers, we can detect 2 T_g s for the mixture: at least one of the two T_g s is different from the T_g of the pure compounds and is located within the range of temperatures between the two T_g s of the pure compounds. The mixture of two completely miscible polymers has a single T_g .

Other experimental methods may be used to reveal the compatibility of polymers such as turbidity measurements, light scattering measurements and infrared measurements (L. A. Utracki, Polymer Alloys and Blends, pp 64-117).

Miscible or compatible polymers are catalogued in the literature, see for example J. Brandrup and E.H. Immergut: Polymer Handbook, 3rd Edition, Wiley & Sons 1979, New York 1989, pp. VI/348 to VI/364; O. Olabisi, L. M. Robeson and M. T. Shaw: Polymer Miscibility, Academic Press, New York 1979, pp. 215-276; L.A. Utracki: Polymer Alloys and Blends, Hanser Verlag Munich 1989.

The lists appearing in these references are given for guidance purposes and are, of course, not exhaustive.

In the same manner as for the diblocks of the prior art, the synthesis of triblocks leads to mixtures, for they contain small quantities of diblocks and manoblocks (homopolymers). Surprisingly, the applicant has found that in the case of triblocks, these by-products were not harmful to the mechanical properties of the composition according to the invention unlike the diblock-based and PVDF- or PVC-based compositions. For these known PVDF- or PVC-based compositions, the presence of these homopolymers is particularly harmful for the properties of the material and thus expensive purification is required.

Thus, the composition according to the invention comprising a copolymer with at least three blocks A, B and C may contain a B-C diblock copolymer and potentially a C homopolymer as by-products of its synthesis.

Likewise, the composition according to the invention comprising a copolymer with at least three blocks A, B and C may contain an A-B diblock copolymer and potentially an A homopolymer as by-products of its synthesis.

Effectively, a copolymer with at least three blocks A, B, C, is preferably synthesized by joining the A block to the B block, then to the C block subsequently or, conversely, the C block to the B block, then to the A block, depending on the nature of the three A, B, C blocks. The A block is by definition the one that is compatible with the compatible thermoplastic resin or resins X_1 to X_n .

Advantageously, the B block is chosen from poly(dienes), particularly poly(butadiene), poly(isoprene) and their statistical copolymers, or from partially or completely hydrogenated poly(dienes) particularly poly(butadiene), poly(isoprene) and their statistical copolymers.

The block copolymer containing at least three blocks A, B and C is such that the A block is connected to the B block and the B block to the C block by means of one or more single covalent bonds. In the case of several covalent bonds between the A block and the B block and/or between the B block and the C block, there may be a single pattern or a sequence of patterns used to join the blocks together.

In the case of a single pattern, it may come from a monomer called a moderator used to synthesize the triblock. In the case of a sequence of patterns, this can be an oligomer resulting from a sequence of monomer units of at least two different monomers in alternating or random order. This type of oligomer can connect the A block to the B block and the same oligomer or a different oligomer can connect the B block to the C block.

Advantageously, the composition according to the invention is characterized in that it contains:

- from 25 to 95%, advantageously at least 50% and preferably 65 to 95% by weight thermoplastic resin or resins X_1 to X_n ,
- the remainder (100%) by weight of the copolymer comprising the three blocks A, B and C connected to one another, these percentages being calculated compared to the total weight of thermoplastic resin(s) with the block copolymers, and in that the block copolymers comprise:
 - 20 to 93 parts by weight of A sequences
 - 5 to 68 parts by weight of B sequences
 - 2 to 65 parts by weight of C sequences.

If the above composition contains several block copolymers each containing the three blocks A, B and C, the quantities indicated above in parts by weight correspond to the sum of all the type A, B and C sequences respectively.

A large number of compounds may advantageously be obtained in accordance with this invention. A non-exhaustive list is indicated below:

- a) a composition that contains by weight:
 - at least 50% and preferably from 65 to 95% poly(carbonate),
 - 100% of the remainder of the triblock copolymer PMMA-PB-PS, these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.
- b) a composition that contains by weight:
 - at least 50% and preferably 65 to 95% poly(carbonate) PC, and
 - 100% of the remainder of the triblock copolymer poly(cyclohexyl methacrylate)-PBS-PS,

these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.

- c) a composition that contains by weight:
 - at least 50% and preferably from 65 to 95% poly(butylenes terephthalate) PET, and
 - 100% of the remainder of the PMMA-PB-PS triblock copolymer,
 these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.
- d) a composition that contains by weight:
 - at least 50% and preferably from 65 to 95% poly(oxyethylene) POE, and
 - 100% of the remainder of the PMMA-PB-PS triblock copolymer,
 these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.
- e) A composition that contains by weight:
 - at least 50% and preferably from 65 to 95% poly(propylene) PP, and
 - 100% of the remainder of the poly(nonyl methacrylate)-PB-PS triblock copolymer,
 these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.
- f) a composition that contains by weight:
 - at least 50% and preferably from 65 to 95% poly(amide) PA,
 - 100% of the remainder of the poly(caprolactone)-PB-PS triblock copolymer,
 these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.

In the case of a fluorinated resin or several compatible fluorinated resins, the composition according to the invention is preferably characterized in that it contains by weight at least 50% and preferably 65 to 95% semicrystalline thermoplastic fluorinated resin(s) and the remainder (100%) by weight of at least one block copolymer with a number-average molecular weight (M_n) greater than or equal to 20,000 g.mol⁻¹ and preferably between 50,000 and 200,000 g.mol⁻¹, consisting of:

- 20 to 93 and advantageously 30 to 60 parts by weight A sequences,

- 5 to 50 and advantageously 10 to 40 parts by weight B sequences,
 - 2 to 50 and advantageously 5 to 40 parts by weight C sequences,
- the percentages being calculated compared to the total weight of fluorinated resin(s) with the block copolymer.

Preferably, the composition includes poly(vinylidene difluoride) PVDF as thermoplastic fluorinated resin and a poly(methyl methacrylate)-poly(butadiene)-poly(styrene) PMMA-PB-PS triblock copolymer.

The compositions according to the invention containing at least 50% and preferably 65 to 95% semicrystalline thermoplastic fluorinated resins have improved shock resistance, elongation at break and an increase in the elasticity limit (stress-strain resistance, absence of necking and whitening during traction) while retaining a high modulus and therefore a certain stiffness and being semicrystalline in nature.

These compositions may be used to produce materials subjected to stresses under high and/or low temperature conditions, in contact with particularly aggressive substances (such as hydrocarbons, strong acids, solvents, mineral and organic bases) during which their resilience properties are particularly required. The preferred compositions are those that contain at least 10% ABC triblock copolymer (compared to the total fluorinated resin(s) + ABC triblock mass).

The fluorinated resin compositions according to the invention as defined above are particularly suited to manufacturing impervious sheaths for flexible metal pipes for extracting and/or transporting gas and hydrocarbons in general in the form of monolayer or multilayer tubes produced via extrusion or co-extrusion in which the flexible metal pipe is then inserted in or molded directly onto the flexible pipe.

In the case of a vinyl resin or several compatible vinyl resins, the composition according to the invention is preferably characterized in that it contains by weight at least 50% and preferably

65 to 95% semicrystalline thermoplastic vinyl resin(s) and the remainder (100%) by weight of at least one block copolymer with an Mn greater than or equal to 20,000 g.mol⁻¹ and preferably between 50,000 and 200,000 g.mol⁻¹, consisting of:

- 20 to 93 and advantageously 30 to 60 parts by weight A sequences,
- 5 to 68 and advantageously 11 to 55 parts by weight B sequences,
- 2 to 50 and advantageously 5 to 49 parts by weight C sequences,

the percentages being calculated compared to the total weight of vinyl resin(s) with the block copolymer.

Preferably, the composition includes poly(vinyl chloride) (PVC) as semicrystalline thermoplastic vinyl resin and a poly(methyl methacrylate)-poly(butadiene)-poly(styrene) triblock copolymer.

Advantageously, the composition includes chlorinated poly(vinyl chloride) (CPVC) as semicrystalline thermoplastic vinyl resin and a poly(methyl methacrylate)-poly(butadiene)-poly(styrene) triblock copolymer.

Compositions containing at least 50% by weight semicrystalline thermoplastic vinyl resin(s) and preferably from 60 to 95%, have improved shock resistance and improved Vicat temperature compared to PVC resins alone or mixed with standard shock additives.

These vinyl compositions can, for example, be used to produce window moldings, tubes, electrical cabinets and boxes, films, plates, and mono- or multilayer bottles.

In the case of a styrene resin or several compatible styrene resins, the composition according to the invention is preferably characterized in that it contains by weight at least 65 to 95% semicrystalline styrene thermoplastic resin(s) and the remainder (100%) by weight of at least one block copolymer with an Mn greater than or equal to 20,000 g.mol⁻¹ and preferably between 50,000 and 200,000 g.mol⁻¹, consisting of:

- 20 to 93 and advantageously 30 to 60 parts by weight A sequences,
- 5 to 50 and advantageously 10 to 40 parts by weight B sequences,

- 2 to 50 and advantageously 5 to 40 parts by weight C sequences, the percentages being calculated compared to the total weight of styrene resin(s) with the block copolymer.

Preferably, the compound includes poly(styrene) as semicrystalline thermoplastic styrene resin and a poly(styrene)-poly(butadiene)-poly(methyl methacrylate) triblock copolymer.

In general, the semicrystalline thermoplastic system resin is syndiotactic.

The composition according to the invention may also contain one or more D thermoplastic polymer(s) compatible with the C sequences, D being present in a quantity of less than 10% of the total X₁ to X_n thermoplastic resin mass and of the block copolymer(s) potentially with its byproducts.

The D polymers can either be homopolymers or statistical copolymers. For triblocks with C sequences derived from styrene, we can cite as D polymer poly(ether phenylene), poly(vinylether) and poly(methylphenylsiloxane).

Advantageously, a method for preparing a material or an object using the composition according to the invention is characterized in that it includes the following steps:

- the thermoplastic resin or resins X₁ to X_n are mixed in melted state with the block copolymer(s) and potentially the D thermoplastic polymer(s) in the presence of any additives and/or charges, which may remain in solid state,
- the liquid or the melted material (with any suspended charges) thus obtained is cooled to produce a solid state material or object.

This method, which consists of mixing the melted resin(s) with the melted copolymer(s), is distinguished by its ease of use. It leads through cooling to a material with a characteristic structure.

The compositions according to the invention result in materials or objects that generally have a

very fine and regular characteristic morphology that can be obtained using the method comprising a simple mixture of the components in melted state and does not require Draconian mixing or dispersion techniques. Furthermore, this morphology is retained for objects formed by injection or extrusion molding of the material (for example in granular form) subjected to another melting, then cooling cycle.

The material or object with a composition according to the invention can be characterized by the following specific heterogeneous structure:

- the structure consists of a continuous phase (matrix) formed essentially of the thermoplastic resins X_1 to X_n containing a discontinuous phase dispersed very evenly as notch formations with a Dn size less than 0.5 micrometer,
- each notch formation contains an internal area consisting mostly or essentially of C blocks and an external peripheral area containing the B blocks of copolymers with at least three blocks A, B and C connected to one another in this order; this peripheral area continuously or discontinuously surrounds the internal area.

Industrial use of the compositions advantageously relies on triblocks with their synthesis by-products. In this case, the morphology changes slightly and we obtain a material or object characterized in that the copolymer with at least three blocks A, B and C contains as synthesis by-products a B-C diblock copolymer and potentially C homopolymer and in that the heterogeneous structure specific to this composition is modified by the fact that the internal notch formation area, consisting mainly or essentially of C blocks, surrounds one or more domains made up essentially of B blocks of the B-C diblock.

Advantageously, the relative weight proportions of semicrystalline thermoplastic resins and triblock copolymers is selected so that the notch formations have a size Dn ranging from 30 to 350 nanometers.

Preferably, the selection is made so that the notch formations have a size Dn ranging from 60 to 250 nanometers.

Generally, the material or object is also characterized in that the distance between two neighboring notch formations Di is between 1.1 and 5 times the size Dn. We note that this distance Di is roughly constant and this indicates a very homogeneous distribution of the notch formations in the material.

This very homogeneous distribution is one of the major advantages of the invention, for it is possible to introduce the block copolymer defined in claim 1 at a very high weight rate without observing any coalescence injurious to the properties of the material or the object.

Among semicrystalline thermoplastic resins we find

- * fluorinated resins known for their good thermal resistance, their chemical resistance, particularly to solvents, adverse weather and radiation (UV, etc.), their gas and liquid impermeability and their electrical insulating quality.

We will cite in particular vinylidene fluoride homo- and copolymers (VF2) preferably containing at least 50% by weight VF2 and at least one other fluorinated monomer such as chlorotrifluoroethylene (CTFE), hexafluoropropylene (HFP), trifluoroethylene (VF3) and tetrafluoroethylene (TFE).

- trifluoroethylene homo- and copolymers (VF2),
- copolymers and particularly terpolymers combining the remaining chlorotrifluoroethylene (CTFE), tetrafluoroethylene (TFE), hexafluoropropylene (HFP) and/or ethylene and potentially VF2 and/or VF 3 patterns

- * polyamide resins or PAs that contain aliphatic and/or cycloaliphatic and/or aromatic patterns.

We can cite the resins obtained by polycondensation of one or more lactams, of α,ω -aminoacids or by a more or less stoichiometric polycondensation of one or more aliphatic diamine(s) and of one or more aliphatic carboxylic diacids.

The preferred lactams are caprolactam, decalactam, undecalactam and dodecalactam.

The preferred α,ω -aminoacids are 6-aminohexanoic, 10-aminodecanoic, 11-aminoundecanoic and 12-aminododecanoic acids.

The carbon chain of the aliphatic α,ω -diamines may be linear (polymethylenediamine) or branched and preferably contains up to 12 carbon atoms. Preferred diamines are hexamethylenediamine (HMDA) and dodecanethylenediamine.

The carbon chain of the aliphatic carboxylic α,ω -diacids may be linear or branched. The preferred diacids are adipic, azelaic, sebacic and 1,12-dodecandioic acids.

As examples of these PA resins, we can mention:

polyhexamethylenedipamide (PA-6,6),
 polyhexamethylenesecbacamide (PA-6,10),
 polyhexamethylenedodecanediamide (PA-6,12),
 poly(tundecanoamide) (PA-11),
 polylaurylactam (PA-12),
 polydodecanethylenedodecanediamide (PA-12,12)
 the copolymers of the preceding.

PAs have a number-average molecular weight M_n that is generally greater than or equal to 5,000 $g \cdot mol^{-1}$. Their inherent viscosity (measured at 20°C for a 0.5 g sample in 100 g of meta-cresol) is generally greater than 0.7.

* polyolefins and particularly polyethylene (PE), polypropylene (PP), polyisoprenes, poly-1 butene, the copolymers of olefins such as PP/PE and PP/polyisoprene;

* vinyl resins having a certain degree of crystallinity and particularly polyvinyl chloride (PVC) with syndiotactic segments, chlorinated PVC (CPVC) and vinyl polychloride (VPC), syndiotactic PS, potentially copolymerized;

* polyesters, particularly polyethylene terephthalate (PET) and polybutylene terephthalate (PBT);

* polycarbonates (PC) among which we can cite poly(oxy-carbonyloxy-1,4 phenylene isopropylidene-1,4 phenylene), poly(oxy-carbonyloxy-1,4 phenylenemethylene-1,4 phenylene) and poly(oxy-carbonyloxy-1,4 phenylene-thio-1,4 phenylene);

* polyoxyalkylenes and particularly polyoxymethylenes (POM), polyoxyethylenes (POE) and polyoxypropylenes (POP);

* aliphatic polyketones, particularly alternating (ethylene ketone) copolymers and terpolymers (ethylene-ketone-propylene).

As an example of A sequences compatible with the homo- and copolymers of VF2, PVC, CPVC, POE and PC, we will cite in particular those derived from alkyl (alkyl)acrylate and, for example, from methyl methacrylate (MMA) and/or from methyl acrylate and/or those derived from vinyl acetate. Advantageously, PMMA sequences, particularly syndiotactic, are preferred. We can also cite the statistical copolymers of butadiene and acrylonitrile containing 23 to 45% acrylonitrile, the statistical copolymers of ethylene and vinyl acetate containing 65 to 75% vinyl acetate and the statistical copolymers of styrene and acrylonitrile containing 28% acrylonitrile that are compatible with PVC.

As examples of A sequences compatible with PA resins, we will cite more particularly those derived from caprolactone and/or glycidyl methacrylate and/or (meth)acrylic acid. We can also cite the statistical copolymers of p(2-hydroxyhexafluoroisopropyl)styrene and styrene that are compatible with PA-6 and PA-12.

As examples of A sequences compatible with polypropylene, we will cite those derived from nonyl methacrylate.

As examples of A sequences compatible with polyesters and polyoxymethylenes, we will cite those derived from alkyl (meth)acrylate(s).

As examples of A sequences compatible with polycarbonates, we will cite those derived from methyl methacrylate.

Among the B sequences, we can cite the polymers obtained from alkyl acrylates such as, for example, butyl acrylate, 2-ethyl hexyl acrylate or preferably dienes, such as butadiene, isoprene,

partially or completely hydrogenated, and particularly advantageously, those with the lowest T_g for example polybutadiene-1,4 with a T_g (around -90°C) lower than the T_g of polybutadiene-1,2 (around 0°C).

Among the C blocks or sequences of ABC triblock copolymers, we can cite the sequences derived from vinylaromatic compounds such as styrene, α-methyl styrene, vinyltoluene, and those derived from alkyl esters of acrylic and/or methacrylic acids having 1 to 18 carbon atoms in the alkyl chain.

Triblocks that contain sequences derived from alkyl (alkyl)acrylate can be prepared by anionic polymerization, for example, in accordance with the methods described in patent applications EP 524,054 and EP 749,987.

The compositions according to the invention may also contain various organic or mineral, macromolecular or not, additives and/or charges and/or coloring agents and/or pigments that are well known in the literature.

As non-exhaustive examples of insoluble charges in these compounds, we can cite mica, alumina, talc, titanium dioxide, carbon black, glass fibers, carbon and macromolecular compounds.

As non-exhaustive examples of additives, we can cite anti-U.V. agents, flame-retardant agents, transformation agents or processing aids.

The sum of these various additives and charges in general represents less than 20% of the total thermoplastic resin(s) + triblock(s) weight.

For example, in the multilayer impervious sheaths described in patent US 5,601,893, the polymer may advantageously be replaced by a fluorinated composition according to this invention.

These compositions are also well suited for use as chemical engineering parts, particularly in the form of pipes, tubes and to produce objects in the building and public works field, such as cable sleeves, guy lines, as well as films and mono- or multilayer sheets for any type of industry. These compounds may be extrusion-blow molded to produce films.

As examples of sheaths, yarns, strands and guy lines, we will cite those described in patent applications EP 671,502 and EP 671,746 where the polymer may be replaced by a composition according to this invention.

These fluorinated compositions are resistant to deformation under stress and the drop in modulus below the elasticity limit is reduced and in some cases even eliminated, which allows them to be used to produce items and materials requiring stress deformation during molding. This is typically the case for renovating natural gas distribution system lines where tubes are jacketed with plastic material and can then be inserted into the existing lines, which are generally made of metal.

The PA resin-based compositions according to the invention may advantageously be used to produce items for the automobile industry, the building industry, sports and recreational activities (piping, tubes, bumpers, body parts, technical parts, molded and thermoformed plates, powders for covering substrates, etc.).

In addition to the description above, the following experimental part with the appended photographs will give a better understanding of this invention. The examples are given purely for the purposes of illustration and do not limit the invention.

EXPERIMENTAL PART

The photographs were taken via electronic microscopy with selective marking of the double bonds present in the polymers. In these photographs, the character μ means micrometer (μm). These photographs appear in the following figures:

- | | |
|-----------|---|
| Figure 1: | Morphology of the material obtained in example 1 |
| Figure 2: | Morphology of the material obtained in example 2 |
| Figure 3: | Morphology of the material obtained in example 3 |
| Figure 4: | Morphology of the material obtained in comparative example 6 (test 2) |
| Figure 5: | Enlargement of Figure 1 |
| Figure 6: | Enlargement of figure 2 |

Figure 7:

Morphology of the material obtained in example 7, test 9, table 9

Figure 8:

Morphology of the material obtained in example 7, test 4, table 9

Figure 9:

Morphology of the material obtained in example 9, test 6, table 12

Figure 10:

Morphology of the material obtained in example 9, test 6, table 12 after shock damage

Figure 11:

Elongation curve of the materials of example 8

Protocol for studying the materials via electronic microscopy

A small sample is taken from a material or object that has been formed from a composition according to the invention or from a composition that is not part of the invention (for comparison).

On this sample, a cut between 40 and 60 nanometers is made using an ultramicrotome. Depending on the stiffness of the sample and in order to get a quality cut, it may be necessary to chill the sample to be cut to -100°C.

If the B blocks result from the polymerization of dienes like butadiene or isoprene, for example, the monomeric patterns of these B blocks contain double bonds that react with osmium tetroxide (OsO₄)

The cut obtained is exposed to OsO₄ vapor for 15 to 30 minutes. This exposure makes it possible to selectively mark the location of the nanodomains formed of poly(diene). After treatment, the cut is observed using a transmission electron microscope. The nanodomains made up of B blocks appear dark against a light background.

When C blocks comprise phenyl radicals, particularly for poly(styrenes), the corresponding nanodomains appear light gray compared to the lighter background corresponding to domains that are inert to OsO₄.

Other selective marking techniques for different polymers for electronic microscopy examination are known in the literature. Thus, it is possible to refer to the different methods described on page 108 of the work *Polymer microscopy* (L.C. Sawyer and D.T. Grubb, Edition Chapman and Hall, London, New York, 1987).

In the case of B blocks formed of a completely hydrogenated poly(diene), they can no longer be revealed by OsO₄. On the other hand, it is possible to mark the Phenyl groups of poly(styrene) that in certain cases form C blocks or A blocks using ruthenium tetroxide.

Thus, depending on the marking techniques used, the three types of domains corresponding respectively to the matrix plus the compatible A blocks, the B blocks and the C blocks may appear in electronic microscopy with different contrasts.

Thus, for example, to reveal a multiphase structure containing a polyamide and a polyolefin, we can use selective marking of the polyamides by means of phosphotungstic acid.

The commercial products (ELF ATOCHEM) sold under the KYNAR® brand are PVDF-based homopolymers or copolymers:

KYNAR® 400 is available in powder form; its melting temperature is 170°C

KYNAR® 710 is a homopolymer available in granular form; its melting temperature is 170°C and its viscosity measured with a capillary rheometer at 230°C and 100 S⁻¹ is 600-750 Pa.s.

KYNAR® 720 is a homopolymer

T_m = 170°C

V = 750-1050 Pa.s under the same conditions as above.

KYNAR® 740 is a homopolymer

T_m = 170° C

V = 1750-2150 Pa.s measured as above.

A triblock denoted by PMMA-PM-PS corresponds to a Poly(methyl methacrylate-*b*-butadiene-*b*-styrene) triblock terpolymer.

Example 1

An ABC triblock denoted by PMMA-PB-PS (50/15/35) for which the Mn of the PMMA sequences is 50,000 g mol⁻¹, the Mn of the PB sequences is 15,000 and the Mn of the PS blocks is 35,000 is prepared according to the method described in EP 524,054 or in EP 749,987.

The crude triblock resulting from anionic synthesis is purified by means of solid-liquid extraction using cyclohexane as selective solvent for the poly(styrene)-poly(butadiene) diblock, the triblock being virtually insoluble under cyclohexane reflux conditions.

A precise quantity of crude triblock is weighed, then placed in a Soxhlet extraction cartridge. Then standard extraction is performed. At the end of extraction, the purified triblock is contained in the cartridge and the poly(styrene)-poly(butadiene) diblock is contained in the cyclohexane. The diblock is recovered via evaporation of the cyclohexane.

As for the purified triblock, the vitreous transition temperature of the PB sequences, mostly having a 1,4 structure, is also -90°C. The PMMA blocks, mostly syndiotactic (>70%) have a Tg of 130°C.

30 parts by weight of this purified ABC triblock are then plasticated for 4 minutes at 215°C in a Brabender mixer with 70 parts by weight PVDF homopolymer sold under the trade name KYNAR® 710 with melt fluidity index (MFI) of 20 cm³/10 min. measured using standard ISO 1133 at 23°C under a 5 kg load. The mixture obtained is calendared, then pressed at 200°C to produce a material in the form of plates 1 mm thick.

The tensile strength (elongation at break), the stiffness, the appearance and the elongation at break are evaluated in accordance with the conditions indicated below:

♦ Tensile strength (elongation at break)

The elongation at break (e_g) of the material and of the KYNAR® 710 alone and the triblock alone are measured according to standard ISO R 527. At ambient temperature, the elongation at break e_g of the composition is equal to 400-450%, while the elongation at break e_g of the KYNAR® 710 measured alone

under the same procedural conditions is equal to 130% and that of the triblock alone is equal to 6%. No whitening is observed beyond the elasticity limit of the composition which is not damaged: no cavities are formed and the deformed area is transparent.

♦ Stiffness/Thermal resistance

The elasticity modulus of the mixture (1500 MPa) is higher than the elasticity modulus of the KYNAR®710 (1,200 MPa) at ambient temperature up to 60°C; on the other hand, above 60°C, the PVDF alone with an elastic modulus of 200 MPa is stiffer than the mixture according to the invention, whose elasticity modulus is 150 MPa.

♦ Visual appearance

The plates produced with the PVDF-triblock mixture plates are transparent while the KYNAR® 710 plates of the same thickness are cloudy.

♦ Examination of the material's morphology (see Figure 1)

On a sample of the material, a cut from 40 to 60 nanometers (nm) thick is made using an Ultramicrotome. This cut is exposed to osmium tetroxide vapor for 15 to 30 minutes, and the cut thus treated is then observed using a transmission electron microscope at magnification level of 30000. The photograph of the image observed is given in Figure 1: the dark color domains smaller than 0.02 µm are formed of B blocks incompatible with the light colored matrix made up of the PVDF + PMMA blocks mixture. The dark B domains form a discontinuous circle around lighter microdomains consisting of PS blocks between 0.05 and 0.07 µm in size. We note that the dispersion of these multiphase PB and PS notch formations in the matrix is very fine and very even.

♦ Fold resistance

The fold resistance of the material obtained is evaluated by manually folding an ISO1/2 specimen 2 mm thick perpendicular to its thickness. We note that the specimen does not whiten at the fold, which is not the case of a same size sample of KYNAR® 710.

♦ Chemical resistance

The ABC triblock is soluble at 23°C in toluene, while the compound prepared previously and placed in toluene for 40 days at 23°C only swells slightly (2% increase in mass).

Example 2

The ABC triblock PMMA-PB-PS (50/15/35) of example 1 is mixed with a PVDF homopolymer sold under the trade name KYNAR®720 (MEI = 10 cm³/10 min. measured according to standard ISO 1133 at 230°C under a load of 5 kg), in the following weight ratios:

- Test 1: Triblock/KYNAR® 720 mixture (07/93)
- Test 2: Triblock KYNAR® 720 mixture (15/85)
- Test 3: Triblock/KYNAR® 720 mixture (22/78)
- Test 3: Triblock/KYNAR® 720 mixture (30/70)

The mixtures are produced in a ZKS twin-screw extruder at 240°C; they are semicrystalline and their melting temperature is roughly equal to that of pure PVDF (170°C). The granules obtained are injected onto a Mining press at 230°C either in the form of 2 mm specimens or in the form of bars 4 mm thick, and their mechanical properties are measured:

♦ Stiffness

The flexural elasticity modulus E is measured during three-point flexion according to standard ISO 178-93 at 23°C.

♦ Resistance to major deformations

The measurement is taken on an ISO1/2 (2mm thick) specimen with an Instron traction machine at a speed of 25 mm/min. at a temperature of 23°C according to standard ISO R527. The deformation of the specimen is monitored using a laser extensometer. Each test is performed on at least five different specimens. The following are measured for each of them:

- Elongation at the elastic limit: ϵ_y
- Stress at the elastic limit: σ_y
- Elongation at break: ϵ_B
- Tensile strength: σ_B
- ♦ Shock resistance

The measurement is taken on an instrumented Charpy impact machine, MGV ZWIK REL 1852 at 23°C, distance between supports 60 mm, at different impactor speeds: 1 and 2 m.s⁻¹. The measurement is taken on unnotched 4.4x9.7x80mm bars. The measurable quantity measured is the energy dissipated by the sample at break, expressed in joules. If the impact does not cause the bar to break, the material is said to be non-breaking (NB).

For purposes of comparison, the same tests were performed on samples of KYNAR® 720 (Control 1). All of the results are given in table 1.

Table 1

Test No.	E (Mpa)	E _y (%)	σ_y (MPa)	$\epsilon_{0.05}$	σ_B (MPa)	E Shock (Jm/g)	E Shock (2m/s)
Control 1	1,580	8.5±0.5	48±1	110±10	37±2	8.2±0.5	6.5±0.5
Test 1	1,460	10±0.5	41±1	280±10	41±2	3.6±0.5	x
Test 2	1,460	11.5±0.5	37±1	260±10	49±2	3.7±0.5	x
Test 3	1,400	13±0.5	35.5±1	235±10	47±2	NB	10.6±0.5
Test 4	1,400	12±0.5	31±1	210±10	45±2	NB	NB

NB: sample did not break

We assess the influence of the temperature on elongation at break ϵ_B of the composition of test No. 4 and on the PVDF alone. The results are given in table 2.

Table 2

Test No.	ϵ_B at 20°C (%)	ϵ_B at 0°C (%)	ϵ_B at -10°C (%)
Control 1	100±10	22±4	21±5
Test 4	200±10	147±5	68±15

The influence of aging on the materials is evaluated by postcuring the samples at 120°C for 15

hours. The elongation at break is measured at 23°C before and after postcuring. The results are given in table 3.

Table 3

Test No.	e_0 before postcuring (%)	e_0 after postcuring (%)
Control 1	110±10	65±10
Test 1	280±10	85±10
Test 2	260±10	110±10
Test 3	235±10	250±10
Test 4	210±10	230±10

The specific volume (V_{spec}) of materials 1 to 4 and of the control is measured at 230°C and at 30°C and the volumetric shrinkage is calculated (specific volume at 230°C/specific volume at 30°C*100). The results are given in table 4.

Table 4

Test No.	V_{spec} at 230°C (cm ³ /g)	V_{spec} at 30°C (cm ³ /g)	Shrinkage (%)
Control 1	0.6764	0.5624	16.8
Test 1	0.6963	0.5838	16.3
Test 2	0.7085	0.597	15.7
Test 3	0.7463	0.6394	14.3
Test 4	0.7637	0.6576	13.9

- ♦ Stability of the material (non-exudation of the triblock)

Using a Perkin Elmer TGA7 thermogravimetric analyzer, we determined the change in weight

for 20-mg pieces taken from test specimens 1 to 4 after 1 hour at 200°C in air; the change was less than 1%.

For the purposes of comparison, we measured the weight change of a specimen piece with the same weight made of up 90 parts by weight KYNAR 720 and 10 parts by weight Butylbenzenesulfonamide (BBSA (plasticizer); its change was equal to 10%.

- ♦ Examination of the material's morphology (see Figure 2)

The examination using the transmission electron microscope (TEM) at a magnification of 30,000 of a cross-section of the test 1 composition (which underwent the exact same treatment as described in example 1) and that contained only 7 parts by weight triblock, also shows a fine and even dispersion of PB notch formations measuring less than 0.02 µm in the PVDF + PMMA blocks matrix.

The size of the notch formations D_n is identical to that of the mixture with more of the same triblock of example 1 (see Figure 1).

The distance between notch formations D_i is greater than the distance for example 1, for the number of notch formations by unit of volume is much lower.

The dark B domains more or less continuously surround much lighter microdomains consisting of PS blocks whose size is between 0.05 and 0.07 µm. We note that the dispersion of these multiphase PB and PS notch formations in the matrix is very fine and very homogeneous. The corresponding photograph is given in Figure 2.

Example 3 (see Figure 3)

In a ZKS twin-screw extruder at 240°C, we mixed 25 parts by weight of the ABC triblock PMMA-PB-PS (50/15/35) of example 1 and 65 parts by weight KYNAR® 720 and 5 parts by weight of a B-C diblock; this PB-PS diblock (30/70) is a by-product of the anionic polymerization of the ABC triblock and consists of a PB block with an M_n of 15,000 g.mol⁻¹ and a PS block with an M_n equal to 35,000. The mixture obtained is semicrystalline, and its melting temperature is roughly equal to that of pure PVDF (170°C). The granules obtained are injected onto a Mining press at 230°C either in the form of 2-mm specimens or in the form of bars 4mm thick and whose mechanical properties and chemical

resistance are measured. The results obtained are roughly identical to those for the material of test No. 4, example 2.

On a sample of the material, a 40 to 60 µm cut is made using an Ultramicrotome. This cut is exposed for 15 to 30 minutes to osmium tetroxide vapor, and the cut thus treated is then observed using the transmission electron microscope at a magnification power of 50,000. The photograph of the image observed is presented in Figure 3: the dark notch formations smaller than 0.02 µm are made up of B blocks incompatible with the light colored matrix formed by the PVDF + PMMA blocks mixture. Some of these B blocks are contained in an external peripheral area of each notch formation and discontinuously surround the internal area of the module, which can be seen in gray. Other B blocks are located inside this internal area. We can reasonably assume that these last B block nanodomains come from the B-C diblocks: Poly(butadiene-*b*-styrene) through comparison with the morphology obtained in example 1 where the triblock does not contain B-C diblocks. In effect, the B-C blocks have more affinity with the C blocks of the internal area of the modules than the A-B-C triblocks, which are drawn toward the matrix by the A blocks compatible with this matrix.

We note an equally fine and homogeneous dispersion of the notch formations within the matrix as for the compositions according to the invention that do not contain any B-C diblocks.

Example 4

We prepared an PMMA-PB-PS (58/11/31) ABC triblock for which the Mn of the PMMA sequences is 58,000 g.mol⁻¹, the Mn of the PB sequences is 11,000 and the Mn of the PS blocks is 31,000 according to the method described in EP 524,054 or in EP 749,987.

We mixed this triblock with KYNAR® 720 and a C-B-C triblock PS-PB-PS (15/70/15) with an Mn of 100,000 g.mol⁻¹ under the procedural conditions of example 2.

The resistance of the materials obtained to the V-notch Charpy shock test was measured at 23, 0 and -10°C with an impact velocity of 1 m.s⁻¹ as indicated in example 2.

The weight proportions of the components (PVDF, A-B-C and C-B-C) of each of the materials tested and the results of the shock resistance test at 23, 0 and -10°C are given in table 5

Table 5

Test No.	mPVDF	mABC	mCBC	m(CBCx100) m(PVDF + ABC)	m(ABC + CBC) m(ABC + CBC)	Shock resistance		
						23°C	0°C	-10°C
Control 2	100	0	0	0	0	B	B	B
Test 5	75	25	0	0	2.75	NB	B	B
Test 6	75	18.75	6.25	6.7	6.2	NB	NB	NB
Control 3	75	13.25	11.75	15	9	NB	NB	B
Test 7	85	7	8	8.7	6.2	NB	B	B

Example 5

25 parts by weight of the triblock of example 2 were mixed with 75 parts by weight semicrystalline PVC sold under the trade name GB 1150 in a Haake twin-screw extruder at 190°C. Using a slot die placed at the output of the extruder, strips 4 mm thick and 35 mm wide were extruded from which specimens are taken to evaluate the softening temperature under load (Vicat temperature) according to standard ISO 306-94 on 5 samples and the corresponding standard deviation was calculated along with the shock resistance according to standard ISO 179-93.

For the purposes of comparison, the Vicat temperature and the shock resistance of the PCV resin alone (Control 4) was measured under the same conditions. The results are given in table 6.

Table 6

Test No.	T _{1/2} at 50 N (°C)	Standard deviation (°C)	R shock at 23°C (kJ/m ²)
Control 4	79.9	0.4	4
Test 8	86.1	0.5	5

Comparative example 6 (see Figure 4)

The following tests show the major disadvantage of the presence of a homopolymer, which is the usual by-product of the synthesis of a diblock.

The poly(butadiene)-poly(methyl methacrylate) PB-PMMA diblock without any notable presence of homopolymer was obtained using the same synthesis process as for the PS-PB-PMMAA triblock. It has an Mn of 100,000 g.mol⁻¹ and is composed of 50% PMMA and 50% PB in number of moles. The homopolymer PB was separated via solid-liquid extraction with cyclohexane as solvent.

The material consisting of 70% PVDF, 25% diblock PB-PMMA + 5% PB homopolymer was obtained in the same way as in the previous examples.

We measured the elongation at break of the materials in table 7 with the following results:

Table 7

Comparative Tests No.	Compositions % by weight	Elongation at break according to the ISO test
1	100% PVDF	50%
2	75% PVDF + 25% PB-PMMA diblock	> 200%
3	70% PVDF + 30% PB-PMMA diblock	> 200%
4	70% PVDF + 25% PB-PMMA diblock + 5% PB homopolymer	10%

Test No. 4 shows the loss in elongation resistance caused by the presence of 5% poly(butadiene). The morphology of test No. 2 appears in Figure 4. We note uniformly filled black or dark notch formations. This coloring corresponds to the marking of the Poly(butadiene) blocks by the osmium tetroxide.

These PB blocks therefore form the interior of the notch formation.

Example 7 (See Figure 7 and 8)

Different PMMA-PB-PS triblocks were prepared according to the process described in EP 524054 or EP 749987. Their characteristics are reported in table 8.

Table 8

Product	% PMMA by weight	% PB by weight	% PS by weight	Total % by weight	Mn	Ip
ABC1	36	28	35	99	80,400	1.7
ABC2	31	22	46	99	100,000	1.9
ABC3	34	31	35	100	113,300	1.8
ABC4	50	29	21	100	90,000	2.2
ABC5	33	36	31	100	80,000	2.0

The molar mass Mn of each triblock was measured by steric exclusion chromatography, and the values were expressed in g.mol⁻¹ in polystyrene-equivalent. The polymolecularity index Ip is defined as the ratio of the molecular weight by weight over the molecular weight by number, or Mw/Mn.

The weight fractions in PMMA, PB and PS are determined by NMR. These products contain a fraction of B-C (PS-PB) diblock and of C (PS) homopolymer. B-C and C are synthesis intermediates. They never represent more than 25% of the final product.

In all cases, the vitreous transition temperature of the PB block is -90°C . The PMMA sequences are more than 70% syndiotactic. The PMMA block has a T_g of 135°C .

Preparation method

In a ZKS twin-screw extruder between 230°C and 240°C , one of the five ABC triblocks above was mixed with a commercial PVDF from Elf Atochem. The compositions of the different mixtures produced are given in table 9 below.

The granules obtained were injected onto a mining press in the form of $80 \times 10 \times 4 \text{ mm}$ bars whose mechanical properties were measured. In particular, the shock resistance was measured using the CHARPY V-NOTCH SHOCK test at different temperatures according to ISO 179/93-1eA.

Table 9

Material	Composition	Average Resilience (kJ/m^2)				
		23°C	0°C	-10°C	-20°C	-30°C
Control 1	Kynar 740	10.6 F	10 F	9.6 F	9 F	6.6 F
Test 1	Kynar 740/ABC1	31.5	15 F	15 F	12.6 F	11.6 F
Test 2	Kynar 740/ABC1	47	26	16 F	13.6 F	12.4 F
Test 3	Kynar 740/ABC1	55	55	52	22	16 F
Test 4	Kynar 740/ABC1	55	55	52	49	18 F

Test 5	Kynar 740/ABC2	85/15	32	15 F	15 F	14 F	12 F
Test 6	Kynar 740/ABC2	75/25	36	32	19	17 F	15 F
Test 7	Kynar 740/ABC3	85/15	51	18	15 F	14 F	11 F
Test 8	Kynar 740/ABC3	75/25	54	53	42	21	15 F
Test 9	Kynar 740/ABC4	80/20	45	45	40	17	13 F
Test 10	Kynar 740/ABC5	85/15	37	37	33	16	12 F
Test 11	Kynar 740/ABC5	80/20	37	35	33	23	12 F
Test 12	Kynar 740/ABC5	75/25	39	38	37	32	22
Control 2	Kynar 400		30	17	15 F	15 F	12 F
Test 13	Kynar 400/ABC1	80/20	98	95	85	80	60

The values indicated with an "F" correspond to the samples that have a brittle fracture. The other samples have a ductile fracture.

Comparison of tests 1 to 13 with control 1:

It must be noted that increased shock resistance is obtained with all the ABC triblocks tested.

Comparison of tests 1, 2, 3 and 4, comparison of tests 5 and 6, comparison of tests 7 and 8 and comparison of tests 10, 11 and 12;

We note that improvement is greater as the triblock content increases to the 10 to 25% range. This is expressed by a shift towards the low temperatures of the ductile/brittle transition. This property is essential for numerous applications.

Modulus/Shock loadoff:

Normally, improved shock resistance is achieved to the detriment of the modulus.

It is remarkable that this improvement in the shock resistance of PVDF is obtained without any significant decrease (<10%) in the flexion modulus of the PVDF and without any drop in the material's melting temperature (<3°C).

It should be noted that, for the first time to the applicant's knowledge, a material consisting of more than 80% PVDF (test 14), having a modulus roughly equal to PVDF and a melting temperature roughly equal to the PVDF exhibits ductile behavior in the V-Notch Charpy Shock test at -30°C.

Morphology:

All these materials have a characteristic morphology.

Figure 8 corresponds to test 4. We note that in the notch formations, PB blocks appear to be revealed inside an internal area consisting primarily of C blocks and that is surrounded by a continuous external peripheral area forming a kind of black ring containing the PB blocks of the triblocks. In contrast to example 1 in which the triblock does not contain any diblocks, the examination of the morphologies confirms that the PB blocks situated inside the notch formations are attributable to the PS-PB diblocks.

Figure 7 corresponds to test 9. It shows a morphology analogous to that of test 4 at a higher magnification power.

The regularity of the domains may be slightly altered during transformation (shear effect).

Remark concerning transformation (ease of obtaining these materials):

Quite surprisingly, we found that the properties of the materials obtained are not dependent on

the state of the products before mixing. Thus, by mixing PVDF granules and a triblock powder, we obtain the same results as if we mix a PVDF powder and a triblock powder, or a PVDF powder and triblock granules or PVDF granules and triblock granules.

Example 8

In a ZKS twin-screw extruder between 230°C and 240°C, an ABC triblock is mixed with a commercial PVDF from Elf Atochem. The compositions of the different mixtures produced are given in table 8.

The granules obtained are injected onto a mining press in the form of ISO 1/2 specimens (2mm thick), and their tractive behavior is measured. The deformation of the specimen is checked using a laser extensometer, the traction speed is 25mm/min., the temperature is kept at 23°C. The stress-strain curves are represented in figure 11 and the main results are indicated in table 10.

Table 10

Material		Composition	ϵ_r (%)	Tractive behavior
Control 1	Kynar 740			Comments
Test 1	Kynar 740/ABC4	85/15	60	Very marked necking
Test 2	Kynar 740/ABC4	80/20	70	Very slight necking
Test 3	Kynar 740/ABC4	70/30	130	No necking. No detectable elasticity limit, homogenous deformation
	Kynar 740/ABC4		200	No necking, elasticity limit barely detectable, homogenous deformation

Comments:

The addition of ABC triblock to PVDF completely changes its tractive behavior. A material that demonstrates no necking and that is homogeneously deformed is obtained. This property is essential for

numerous applications where the appearance of damage (necking) beyond 10% elongation is harmful. It is surprising that this change in tractive behavior is obtained without any significant reduction of the material's modulus.

Production of films:

Using ABC + PVDF granules, films were produced on a Randcastle RCP0500 microextruder. The temperature profile was set at 210°C in the first two heating zones and at 185°C in the die. Films whose thickness can be controlled to between 10µm and 400µm were obtained.

Traction tests on these films were performed. The PVDF film (Kynar 740) necks, while the films obtained by mixing Kynar 740 with 15% ABC1 and the films obtained by mixing Kynar 740 with 15% ABC4 do not exhibit any necking, and their deformation is homogeneous. This property is important for film applications or for bubbles in extrusion-blow molding.

It also makes it possible to produce products for producing coextrusion binders.

Measurements of volatile oil and solvent permeability

Using the films produced previously, measurements of permeability resistance to volatile oils, methanol and toluene were taken. We noted that the ABC+PVDF materials retain excellent barrier properties.

The combination of these excellent barrier properties, of the particular tractive behavior (no necking) and the excellent shock properties make ABC+PVDF materials perfectly suited to producing tubes (monolayer or multilayer) or extruded or molded parts used to transport or store volatile oils, organic solvents or aggressive fluids.

Example 9: PVC + PMMA-PB-PS triblock

The addition of ABC triblock to PVC facilitates its transformation. This can be shown by measuring the time necessary to obtain an evenly melted sheet on a twin-cylinder counter-rotating

calender (the melting time is noted). Furthermore, the addition of ABC triblock to a material whose shock resistance (measured according to standard ISO 179/93-1EA) and Vicat Point (measured according to standard ISO 306/94-B50) are improved. This result is completely surprising. Indeed:

- standard PVC shock additives such as coreshell rubber (MBS) and acrylic coreshells result in a reduction of the Vicat point.
- standard PVC "heat" additives improve the Vicat point, but result in a reduction in shock resistance.

Another surprising point is that the improvement of all these properties is not detrimental to the transparency of the material.

Different PMMA-PB-PS triblocks were prepared using the same method described in EP 524,054 or in EP 749,987. Their characteristics are recalled in table 11.

Table 11

Product	% PMMA by weight	% PB by weight	% PS by weight	Mn	Ip
ABC1	36	28	35	80,400	1.7
ABC4	50	29	21	90,000	2.2

Effect on transformation

Several grades of commercial PVC from Elf Atochem were used. Their Kwert varies between 57 and 70. These products were pre-formulated with 2 parts thermal stabilizer, 1.9 parts external lubricants and 1.5 parts processing aid. Different dry mixtures were produced with the same weight composition: 75% preformulated PVC and 25% ABC triblock.

One of its PVC grades (KW67) was formulated with only 0.6 part lubricant and 2 parts thermal stabilizer (without any processing aid). This is control No. 4. Two mixtures were prepared with 15% and with 25% ABC triblock. The results obtained are given in table 12.

Table 12

Reference	Product	Temperature of the rolls (°C)	Sheet-forming time (min.)
Control 1	PVC KW57	190	12
Test 1	Control 1/ABC4 75/25	190	5
Test 2	Control 1/ABC4 75/25	190	9
Control 2	PVC KW67	200	29
Test 3	Control 2/ABC1 75/25	200	4
Test 4	Control 2/ABC4 75/25	200	12
Control 3	PVC KW70	215	7
Test 5	Control 3/ABC1 75/25	215	4
Test 6	Control 3/ABC4 75/25	215	6
Control 4	PVC KW67	190	> 30
Test 7	Control 4/ABC4 85/15	190	6
Test 8	Control 4/ABC4 75/25	190	5

Comments:

We note that the addition of triblock significantly reduces the product's sheet forming time. This is a major advantage of the formulation according to the invention. Other products have the same effect, but to our knowledge, none has all of the properties of these formulations (use, Vicat, shock resistance).

The addition of ABC triblock to control No. 4 transforms this product at 190°C, while it cannot be transformed at this temperature alone.

Combined improvement of the Shock resistance properties and the Vicat point

With the same protocol as described previously, different sheets of PVC+ABC mixtures were produced on two-roll calendar machines. The sheets obtained were press molded into plates 4 mm thick at 195°C for 8 minutes.

80x10x4mm bars are cut from these plates in order to take V-notch Charpy Shock measurements at 23°C according to standard ISO 179/93-1EA. On these plates, Vicat point measurements were taken according to standard ISO 306/94-B50. The results obtained are given in table 13.

Table 13

Reference	Product	Resilience at 23°C (kJ/m ²)	Vicat temperature 50N (°C)
Control 2	PVC KW57	5.5 F	70.5
Test 9	Control 2/ABC4 85/15	20	81.4
Test 10	Control 2/ABC4 80/20	30	82.3
Test 6	Control 2/ABC4 75/25	64	82.9
Test 11	Control 2/ABC4 60/40	25	83.6

The values indicated with an "F" correspond to samples that have a brittle fracture. The other samples have a ductile fracture.

Structure

All these materials have a particular structure as described below.

We have attached a transmission electron microscope plate of a sample taken from a bar corresponding to test 6 (figure 9).

Once again, we show that the structure is an intrinsic characteristic of the materials according to the invention.

The regularity of the domains may be altered slightly during transformation (shear effect).

A transmission electron microscope plate was made of a damaged bar (recovered after the V-notch Charpy shock test). The area observed corresponds to the area where the material was deformed in a ductile fashion (figure 10). We note on this plate that, surprisingly, the deformation is extremely homogeneous. An extremely large number of micro holes were created inside the domains (formed by the

B and C blocks of the ABC triblock. The creation of these holes is a key factor for dissipating energy and therefore for strengthening the material's shock resistance.

Example 10: Chlorinated Poly(vinylchloride) (CPVC) + PS-PB-PMMA triblock

The addition of ABC triblock to CPVC facilitates its transformation. This can be shown by measuring the time necessary to obtain an evenly melted sheet on a two-roll counter-rotating calendar (the melting time is noted). Furthermore, the addition of ABC triblock results in a material whose shock resistance properties (measured according to standard ISO 179/93-1EA) are improved. Depending on the level of chloride in the CPVC, this improvement in the shock properties is produced jointly with an increase or decrease in the Vicat point (measured according to standard ISO 306/94-B50).

Another surprising point is that the triblocks make it possible to obtain shock resistance values that are unparalleled to the applicant's knowledge.

Another surprising point is that the improvement of all these properties has no adverse effect on the material's transparency.

Several grades of CPVC were used. Their Kwert varied between 57 and 67 and the chlorine content varied between 62% and 69%. These products were preformulated with 2 parts by weight thermal stabilizer, 1.9 parts external lubricants and 1.6 parts processing aid. Different dry mixtures were produced with 15% ABC triblock. The results obtained are given in table 14.

Table 14

Reference	Product	Temperature of the rolls (°C)	Sheet formation time (min.)
Control 1	CPVC KW57 65% Cl	200	17
Test 1	Control 1/ABC1 85/15	200	6
Test 2	Control 1/ABC4 85/15	200	6
Test 3	Control 1/ABC6 85/15	200	7

Control 2	CPVC KW57 65% Cl	215	20
Test 4	Control 2/ABC1 85/15	215	3
Test 5	Control 2/ABC4 85/15	215	5
Test 6	Control 2/ABC6 85/15	215	8

With the same protocol as described previously, different sheets of CPVC+ABC mixtures were produced on two-roll calendar machines. The sheets obtained were press molded into plates 4 mm thick at 195°C for 8 minutes.

80x10x4mm bars were cut from these plates in order to take V-notch Charpy Shock test measurements at 23°C according to standard ISO 179/93-1EA. On these plates, Vicat point measurements were taken according to standard ISO 306/94-B50. The results obtained are given in table 15.

Table 15

Reference	Product	Resilience at 23°C (kJ/m2)	Vicat temperature 50 N (°C)
Control 1	CPVC KW57 65% Cl	2.7 F	102.9
Test 7	Control 1/ABC1 75/25	48.5	102
Test 8	Control 1/ABC6 75/25	8.7	104.2
Control 2	CPVC KW67 65% Cl	3.1 F	106.4
Test 4	Control 2/ABC1 85/15	9.3	103.4
Test 5	Control 2/ABC4 85/15	17.5	104.6
Control 3	CPVC KW57 62% Cl	3.2 F	90.3
Test 9	Control 3/ABC1 75/25	63.3	91.3
Test 10	Control 3/ABC6 75/25	8.5	94.4
Control 4	CPVC KW57 67% Cl	1.9 F	113.3
Test 11	Control 4/ABC1 75/25	23.6	107.1
Test 12	Control 4/ABC6 75/25	15.3	111.5
Control 5	CPVC KW57 69% Cl	1.8 F	124.5

Test 13	Control 5/ABC1 75/25	13.3	113.6
Test 14	Control 5/ABO6 75/25	10.4	117.6

The values indicated with an "F" correspond to samples that have a brittle fracture. The other samples have a ductile fracture.

Conclusions:

Added to CPVCs with a chlorine content of less than 65%, ABC triblocks make it possible to obtain a material that is easier to transform, whose Vicat point is higher and whose shock properties are exceptional

Added to CPVCs whose chlorine content is greater than 65%, ABC triblocks make it possible to obtain a material that is easier to transform and whose shock properties are excellent.

CLAIMS

1. Composition intended to be formed into a material or an object comprising:

- a semicrystalline thermoplastic resin X_1 or several compatible thermoplastic resins X_1 to X_n at where at least one X_1 is semicrystalline,

- and
 - at least one block copolymer (sequences),
 - n being a whole number equal to or greater than 1,
- characterized in that:

- the block copolymer comprises at least three blocks A, B and C connected to one another in this order, each block being either a homopolymer or a copolymer obtained from two or more monomers, the A block being connected to the B block and the B block to the C block by means of a covalent bond or an intermediate molecule connected to one of these blocks by a covalent bond and to the other block by another covalent bond, and in that

- the A block is compatible with the thermoplastic resin or resins X_1 to X_n ,
- the B block is incompatible with the thermoplastic resin or resins X_1 to X_n , and incompatible with the A block,
- the C block is incompatible with the thermoplastic resin or resins X_1 to X_n , the A block and the B block.

2. Composition as claimed in claim 1, characterized in that the B block has a vitreous transition temperature T_{gB} lower than 23°C.

3. Composition as claimed in claim 1 or 2, characterized in that the T_{gB} of the B block is lower than 0°C.

4. Composition as claimed in claim 1 or 2, characterized in that the T_{gB} of the B block is lower than -50°C.

5. Composition as claimed in one of claims 1 through 4, characterized in that the C block has a vitreous transition temperature T_{gC} or a melting temperature T_{fC} higher than the T_{gB} of the B block.

6. Composition as claimed in one of claims 1 through 5, characterized in that the copolymer with

at least three blocks A, B and C contains as by-products of its synthesis a B-C diblock copolymer and potentially C homopolymer.

7. Composition as claimed in one of claims 1 through 5, characterized in that the copolymer with at least three blocks A, B and C contains as by-products of its synthesis an A-B diblock copolymer and potentially A homopolymer.

8. Composition as claimed in one of claims 1 through 7, characterized in that the B block is chosen from poly(dienes), particularly poly(butadiene, poly(isoprene) and their statistical copolymers, or from partially or completely hydrogenated poly(dienes), particularly poly(butadiene), poly(isoprene) and their statistical copolymers.

9. Composition as claimed in one of claims 1 through 8, characterized in that the A block is connected to the B block by an oligomer resulting from a sequence of monomer units with at least two different monomers in alternating or random order.

10. Composition as claimed in one of claims 1 through 9, characterized in that the B block is connected to the C block by an oligomer resulting from a sequence of monomer units with at least two different monomers in alternating or random order.

11. Composition as claimed in one of claims 1 through 10, characterized in that it contains:

- 25 to 95%, advantageously at least 50% and preferably 65 to 95% by weight of the thermoplastic resin(s) X_1 to X_n
 - the remainder (100%) by weight of the copolymer comprising the three blocks A, B and C connected to one another, the percentages being calculated compared to the total weight of thermoplastic resin(s) with the block copolymer,
- and in that the block copolymer comprises:

- 20 to 93 parts by weight A sequences
- 5 to 68 parts by weight B sequences
- 2 to 65 parts by weight C sequences.

12. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight:

- at least 50% and preferably 65 to 95% poly(carbonate),
 - 100% of the remainder of the PMMA-PB-PS triblock copolymer,
- these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.

13. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight:

- at least 50% and preferably 65 to 95% poly(carbonate) PC, and
- 100% of the remainder of the poly(cyclohexyl methacrylate)-PB-PS triblock copolymer,

these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer,

14. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight:

- at least 50% and preferably 65 to 95% poly(butylene terephthalate) PBT, and
- 100% of the remainder of the PMMA-PB-PS triblock copolymer,

these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.

15. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight:

- at least 50% and preferably 65 to 95% poly(oxyethylene) POE, and
- 100% of the remainder of the PMMA-PB-PS triblock copolymer,

these percentages being calculated compared to the total weight of thermoplastic resin(s) and the block copolymer.

16. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight:

- at least 50% and preferably 65 to 95% poly(propylene) PP, and
- 100% of the remainder of the poly(nonyl methacrylate)-PB-PS triblock copolymer,

these percentages being calculated compared to the total weight of thermoplastic resin(s) and of the block copolymer.

17. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight:

- at least 50% and preferably 65 to 95% poly(amide) PA,
- 100% of the remainder of the poly(caprolactone)-PB-PS triblock copolymer,
- these percentages being calculated compared to the total weight of thermoplastic resins and the block copolymer.

18. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight at least 50% and preferably 65 to 95% semicrystalline thermoplastic fluorinated resin(s) and the remainder (100%) by weight of at least one block copolymer with a number-average molecular weight (Mn) greater than or equal to 20,000 g.mol⁻¹, and preferably between 50,000 and 200,000 g.mol⁻¹, consisting of:

- 20 to 93 and advantageously 30 to 60 parts by weight A sequences,
- 5 to 50 and advantageously 10 to 40 parts by weight B sequences,
- 2 to 50 and advantageously 5 to 40 parts by weight C sequences,

the percentages being calculated compared to the total weight of fluorinated resin(s) with the block copolymer.

19. Composition as claimed in claim 18, characterized in that it includes poly(vinylidene difluoride) (PVDF) as thermoplastic fluorinated resin and a poly(methyl methacrylate)-poly(butadiene)-poly(styrene) triblock copolymer.

20. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight at least 50% and preferably 65 to 95% of semicrystalline thermoplastic vinyl resin(s) and the remainder (100%) by weight of at least one block copolymer with an Mn greater than or equal to 20,000 g.mol⁻¹ and preferably between 50,000 and 200,000 g.mol⁻¹, consisting of:

- 20 to 93 and advantageously 30 to 60 parts by weight A sequences,
- 5 to 68 and advantageously 11 to 55 parts by weight B sequences,
- 2 to 50 and advantageously 5 to 49 parts by weight C sequences,

the percentages being calculated compared to the total weight of vinyl resin(s) with the block copolymer.

21. Composition as claimed in claim 20, characterized in that it includes poly(vinyl chloride) (PVC) as semicrystalline thermoplastic vinyl resin and a poly(methyl methacrylate)-poly(butadiene)-poly(styrene) triblock copolymer.

22. Composition as claimed in claim 20, characterized in that it includes chlorinated poly(vinyl chloride) (CPVC) as semicrystalline thermoplastic vinyl resin and a poly(methyl methacrylate)-poly(butadiene)-poly(styrene) triblock copolymer.

23. Composition as claimed in one of claims 1 through 11, characterized in that it contains by weight at least 50% and preferably 65 to 95% semicrystalline styrene thermoplastic resin(s) and the remainder (100%) by weight of at least one block copolymer whose Mn is greater than or equal to 20,000 g.mol⁻¹ and preferably between 50,000 and 200,000 g.mol⁻¹, consisting of:

- 20 to 93 and advantageously 30 to 60 parts by weight A sequences,
- 5 to 50 and advantageously 10 to 40 parts by weight B sequences,
- 2 to 50 and advantageously 5 to 40 parts by weight C sequences,

the percentages being calculated compared to the total weight of styrene resin(s) with the block copolymer.

24. Composition as claimed in claim 23, characterized in that it includes poly(styrene) as semicrystalline thermoplastic styrene resin and a poly(styrene)-poly(butadiene)-poly(methyl methacrylate) triblock copolymer.

25. Composition as claimed in one of claims 1 through 24, characterized in that it also contains one or more C thermoplastic polymers compatible with the C sequences, D being present in a quantity of less than 10% of the total weight of the thermoplastic resin(s) X₁ to X_n and the block copolymer(s) potentially with its by-products.

26. Method for preparing a material or an object using the composition as claimed in one of claims 1 through 25, characterized in that it includes the following steps:

- the thermoplastic resin(s) X_1 to X_n is (are) mixed in melted state with the block copolymer(s) and potentially the D thermoplastic polymer(s) and in the potential presence of additives and/or charges that may remain in solid state,

- the liquid or the melted material (potentially with the suspended charges) thus obtained is cooled to produce a material or an object in solid state.

27. Material or object having a composition as claimed in one of claims 1 through 25, characterized by the following specific heterogeneous structure:

- the structure is formed of a continuous phase (matrix) formed essentially of the thermoplastic resins X_1 to X_n containing a discontinuous phase dispersed very evenly in notch formations with a size D_n less than 0.5 micrometer.

- each notch formation contains an internal area consisting mostly or essentially of C blocks and an external peripheral area containing the B blocks of the copolymers with at least three block A, B and C connected to one another in this order, this peripheral area surrounding the internal area continuously or discontinuously.

28. Material or object as claimed in claim 27, characterized in that the copolymer with at least three blocks A, B and C contains as by-products of its synthesis a B-C diblock copolymer and potentially C homopolymer and in that the heterogeneous structure characteristic of this composition is modified by the fact that the internal area of the notch formations, consisting mostly or essentially of C blocks, surrounds one or more domains consisting essentially of B blocks of the B-C diblock.

29. Material or object as claimed in claim 27 or 28, characterized in that the notch formations have a size D_n ranging from 30 to 350 nanometers.

30. Material or object as claimed in claim 27 or 28, characterized in that the notch formations have a size D_n ranging from 60 to 250 nanometers.

31. Material or object as claimed in one of claims 27 to 30, characterized in that the distance between neighboring notch formations D_1 is between 1.1 and 5 times the value of the size D_n .

[See Original for Figures 1 - 8]

Morphology before damage
ABC + PVC
Figure 9
[See Original for Image]

Morphology after damage
ABC + PVC
Figure 10
[See Original for Image]

Traction properties of ABC+PVDF materials

ABC4 / KYNAR 740

ISO1/2, 25 mm/min, T_{inj}=80°C, 23°C, Laser extensometer

[See original for graph]

Stress (MPa)

Elongation (%)

Figure 11